SOLVENT EFFECTS IN SUPERCRITICAL EXTRACTION OF COAL

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INTRODUCTION

Supercritical gas extraction is particularly suitable for the recovery of the liquids formed when coal is heated to above 400°C. These liquids are normally too involatile to distill at this temperature. If the temperature is increased, they polymerize to form heavier and larger molecular species and evolve as gases and liquids. Only a relatively small amount of the coal distills as tar from the decomposing material. Supercritical gas extraction affords a means of recovering these liquids as they are formed while avoiding the undesirable decomposition reactions (1). Supercritical fluids have a density of about 30% of that of a normal fluid, which is high enough to provide for good solvent capability, but also low enough for high diffusivity and rapid mass transfer throughout the complex coal matrix.

The use of supercritical fluids for the recovery of hydrocarbons and related compounds from coal was pioneered by the National Coal Board (NCB) in Britain. Over a number of years, NCB has investigated the direct extraction of coals using light aromatic solvents (mostly toluene) under supercritical conditions. In a recent NCB report, Whitehead (2) summarized the experimental data on supercritical extraction of coal, obtained both on bench-scale units and on a 5 kg/h continuous pilot plant operated in Britain by the Coal Research Establishment. According to these data, the residence time of coal under supercritical conditions was the variable which most influenced the extract yield. The influence of pressure and temperature on the yield was also substantial, and an extract yield of 35% by weight of the dry, ash-free coal could be obtained using toluene at 420°C and 27.5 MPa pressure. It was also determined that it was not essential for the extracting fluid to be above its critical temperature to be effective. For a given operating pressure, the advantages of operating in a supercritical state were associated with the lower density and viscosity of the fluid compared with a subcritical fluid.

In another coal-related effort in the United States, Kerr-McGee Corporation has developed a new solid-liquid separation technique utilizing the unique solvent capabilities of supercritical fluids (3). The process, called Critical Solvent Deashing (CSD), is used to separate mineral matter and unreacted coal from coal liquids. A two-stage CSD pilot plant (integrated into an SRC process unit) has been operated for the last four years at Wilsonville, Alabama.

Despite the strong industrial interest and the extensive research activity in the field of supercritical extraction, much remains to be learned in the application of supercritical fluids to coal processing. An important feature of supercritical coal extraction that has received little attention in the literature concerns the specific characteristics (physical and/or chemical) of the supercritical solvent and solvent mixtures that can affect the yield and the quality of the coal extracts. Paul and Wise (4) in their excellent monograph on gas extraction used the semiquantitative approach of Rowlinson and Richardson (5) to show the strong dependence of supercritical solubility on the cross-virial coefficient B_{12} of the solvent-substrate gas phase. They also discussed empirical correlations for calculating these coefficients in relatively simple cases of nonpolar molecules. The existing B_{12} correlations, however, are most likely to prove completely unsatisfactory for polar solvents, or for solvents that are chemically (as well as physically) involved in the mechanism of coal extraction. Polar or hydrogen bonding solvents, for example, may exert a stronger dissociating or depolymerizing action on coal during the thermal fragmentation stage than nonpolar solvents, thus increasing the yield of extractable coal material.

The present paper discusses some results from the first phase of our experimental investigation into solvent and chemical-reaction effects in supercritical coal extraction. The second phase currently under way is concerned with the combination of supercritical extraction and specific chemical treatment of the coal (such as

catalytic depolymerization, alkylation, hydrogen-donor activity, etc.) to increase the yield of coal extracts and decrease the severity of the extraction conditions.

EXPERIMENTAL

All supercritical extraction experiments were carried out in batch mode, in a 1000 cm^3 (free volume:910 cm^3), 316SS AE MagneDrive autoclave equipped with a digital temperature controller/indicator and a digital pressure transducer/indicator in the 0-10,000 psi range (Autoclave Engineers, Model DPS-0201). An Illinois No. 6 bituminous coal, 100x200 mesh size, was used throughout this investigation. Its proximate and ultimate analyses are included in Table 5. The coal was dried under vacuum at 110°C for 24 hours before every run.

In each run a certain amount of solvent, corresponding to the desired supercritical density, was first measured into the autoclave. Then a fine-mesh basket containing 20 grams of the dried and sized coal was suspended at the top of the autoclave, so that no actual contact between the liquid solvent and the coal sample was possible. We took this precaution to eliminate any ambiguity in the results, where a significant fraction of the coal would be soluble under supercritical conditions but insoluble when the system was brought back to ambient conditions, thus precipitating on the extracted coal and causing the extraction yields (which are based on the weight loss of the raw coal) to appear low (6). In our system any material dissolved under supercritical conditions is carried through and recovered outside the basket after the experiment, whether or not this material is still soluble.

After sealing and purging, the reactor was heated for about 1.5 hr to reach extraction temperature (400°C). Following 2 hrs of extraction, the system was cooled to room temperature (2 hrs). Yield was defined as the weight loss of the vacuum dried (24 hrs, 110°C), char-containing basket expressed as a percentage of the raw, dry-coal weight.

The results on weight-percent extraction reported in this paper were reproducible within ±0.5 wt% (absolute). Solvent recoveries after extraction ranged between 96 and 100%. Decreasing the particle size and the amount of coal sample (for a given solvent density), and increasing the extraction time had no effect on extraction yields. Therefore, the reported results reflect a condition of equilibrium extraction with no mass transfer or solvent-saturation limitations.

The extracted coal samples, as well as the supercritical extracts, were analyzed for elemental composition, heating value, and pyridine solubility.

RESULTS AND DISCUSSION

1. Non-polar Sovent Effects

To determine the effect of the physical parameters of the supercritical solvent on coal extraction, coal samples were extracted with a homologous series of n-paraffins (from pentane to dodecane), at 400°C and at a constant solvent density of 2.75 moles/liter. Results on weight-percent extraction and final extraction pressure (which is generated by the supercritical solvent itself) are given in Table 1. The critical parameters of the paraffinic solvents are listed in Table 2.

The results indicate that extraction yield increases with increasing molecular weight of the solvent, dodecane being the best supercritical solvent under the given experimental conditions. On the other hand, extraction pressure displays an interesting behavior, decreasing with increasing molecular weight of the solvent (at constant temperature and molar density), then passing through a minimum (for nonane), and finally increasing with increasing molecular weight.

Based on their experimental results on high-pressure gas chromatography, Giddings et. al. (7) suggested that the solvent power of a supercritical medium is directly related to its solubility parameter, δ. Using the van der Waals equation, they developed the following correlation:

$$\delta\left(\frac{cal}{cm^3}^{1/2}\right)^{3/2} = 1.25 P_c^{1/2} \frac{\rho_r}{\rho_\ell} \qquad 1)$$

where P_c is the critical pressure of the solvent in atmospheres,

ρ_r is its reduced density $\triangleq \frac{\rho}{\rho_{critical}}$, and

ρ_ℓ is the reduced density of liquids, taken to be about 2.66.

It is important to note here that the above correlation is likely to prove satisfactory for non-polar solvents, but its value in predicting solvent capabilities when special solvent effects are present (polar clustering, hydrogen bonding, etc.) is very much in doubt. Blessing and Ross (6), based on a limited number of supercritical extraction experiments on coal and lignite, concluded that the extraction yield is an almost liner, universal (for a given coal) function of the solubility parameter of the solvent as calculated by the Giddings correlation, and that regardless of their structural differences, all compounds largely perform in accordance with their solvent capabilities. This is a rather arbitrary statement, taking into account the fact that only one polar solvent (methanol) was included in their plot of coal extraction versus solubility parameter of the solvent.

Using Giddings' correlation, solubility-parameter values for the homologous series of n-paraffins were calculated at the experimental solvent density of 2.75 moles/liter. The results are given in the last column of Table 2. Weight-percent extraction is plotted against solvent solubility parameter in Figure 1. As can be seen from the figure, the plot is highly linear (correlation coefficient 0.987), yielding the following correlation:

$$(\text{wt\% extraction}) = 3.05\delta + 11.2 \qquad 2)$$

Table 4 includes the results on supercritical coal extraction at 400°C and three different solvent densities, for another nonpolar hydrocarbon solvent, namely toluene. Solubility-parameter values calculated from Giddings' correlation are given in the last column of Table 4. Linear regression on the toluene runs yields the following correlation (correlation coefficient 0.986):

$$(\text{wt\% extraction}) = 3.96\delta + 10.9 \qquad 3)$$

A measure of the accuracy of the experimental results is the predicted value for the extraction yield at the limit $\delta \to 0$ (vacuum pyrolysis of coal), which should be the same for all solvents. Equations 2 (n-paraffins) and 3 (toluene) predict extraction limits very close to each other (11.2 and 10.9 weight percent respectively). However, contrary to the conclusion of Blessing and Ross, the extraction yield depends also on the solvent functionality. By comparing equations 2 and 3 it can be seen that toluene is a better solvent in supercritical coal extraction than straight-chain aliphatic hydrocarbons, for the same value of the Giddings solubility parameter. As we will show later the effect of functionality is even stronger for polar solvents.

It has also been suggested (Fong, et.al, (8)) that extraction yields may be affected by molecular size, and that the longest dimension of each solvent molecule should be considered when comparing the coal extraction efficiencies of various supercritical solvents. The implication here is that penetration of the micropore structure of the coal can be achieved more easily by the smaller molecules. Our results on the homologous series of n-paraffins, where dodecane, the longest molecule, proved to be the most effective extraction solvent, certainly do not support this suggestion. Mass transfer limitations do not appear to be significant in supercritical coal extraction, at least under the given experimental conditions.

The behavior of the extraction pressure at constant temperature and molar density in the homologous series of n-paraffins is worth further consideration from the standpoint of optimizing the extraction conditions. Our results, for example, indicate that n-nonane is a superior solvent than n-pentane in supercritical coal extraction, not only in terms of the higher extraction yield, but also in terms of the considerably lower extraction pressure.

The Redlich-Kwong equation of state

$$P = \frac{RT}{\hat{V}-b} - \frac{a}{T^{1/2}\hat{V}(\hat{V}+b)} \qquad 4)$$

where

$\hat{V}$ = molar volume = $\frac{1}{\rho}$ (ρ = molar density)

$$a = \frac{0.4278R^2T_c^{2.5}}{P_c}, \text{ and}$$

$$b = \frac{0.0867RT_c}{P_c},$$

was used to examine the extraction-pressure trends in the homologous series of n-paraffins, under the given experimental conditions: T = 400°C and ρ = 2.75 moles/liter or $\hat{V} = \frac{1}{\rho} = 363.6$ cm^3/mole. Critical parameters for the n-paraffins, as well as calculated values for a and b, and estimated (eq. 4) values for the extraction pressure are given in Table 2. These data show that, despite the considerable differences between estimated and observed values of the extraction pressure, especially for the higher paraffins, the Redlich-Kwong equation is able to predict the pressure minimum at almost the same solubility-parameter value as the experimental one. The structure of the Redlich-Kwong equation, and the strong dependence of the pressure on the $(\hat{V}-b)^{-1}$ term in particular, suggests a very interesting path for optimizing extraction conditions. In Table 3 we list estimated extraction pressures and solubility-parameter values for the homologous series of n-paraffins, in supercritical coal extraction at 400°C and two other molar densities. As can be seen from the table, by decreasing the molar density, the pressure minimum shifts towards the heavier hydrocarbons, which still possess the higher solubility-parameter values. Thus, by proper selection of the experimental solvent density (1.8 moles/liter in our case), dodecane becomes an excellent supercritical solvent for coal, both in terms of the highest extraction yield in the hydrocarbon series, and also in terms of the lowest generated extraction pressure.

The same solvent density considerations can, of course, be applied to any other homologous series of nonpolar compounds (e.g. aromatic hydrocarbons).

2. Polar Effects in Supercritical Coal Extraction

We are currently conducting an extensive experimental investigation on the effect of increased solvent polarity on coal extraction yields. A wide range of supercritical solvents is being studied, including simple inorganic molecules (CO_2, H_2O, NH_3, BF_3, etc.), and polar hydrocarbons, particularly alcohols. Table 4 gives the results of some preliminary supercritical extraction experiments at 400°C with simple polar compounds, such as methanol, acetone and water.

Methanol gives a slightly lower extraction yield (20.6% versus 21.3%) than estimated from the Giddings correlation and equation 2. From a practical standpoint, however, methanol is far inferior a supercritical solvent than aliphatic hydrocarbons, because it gives lower extraction yields at much higher extraction pressures (20.6% at 3610 psig compared with 21.2% at 1290 psig for n-nonane).

The predictive value of equation 2 when coupled with the Giddings correlation breaks down completely for a polar solvent such as acetone, which shows anomalously low coal extraction yields at 400°C. These low yields can only in part be attributed to acetone decomposition that was experimentally observed at 400°C.

Water, on the other hand, displays large positive deviations from the estimated extraction values. For example, at 400°C and a supercritical density of 8.25 moles/liter the coal extraction yield is 34.0 wt% compared with 20.9wt%, which is the value calculated from equations 1 and 2. The results in Table 4 seem to indicate that water is an even better supercritical solvent than toluene for coal extraction, affecting high extraction yields at moderately high pressures (34wt% at T_r=1.04 and P_r=1.12). A very interesting feature of the supercritical water runs is that the extract-containing aqueous phase, when brought back to ambient conditions is an almost clear, stronly smelling solution with a minimal amount of precipitate, and in any case it is completely different from the black coal solutions obtained in supercritical toluene runs. Whether this is a result of supercritical water extracting selectively a different portion of the coal material (e.g. more of the polar, phenolic fraction) than toluene, or it is mainly a result of high-pressure reforming reactions of coal organics with supercritical water than can yield products completely different from simple supercritical extracts (9), is not clear at this point.

We are currently investigating the mechanism of supercritical water/coal interactions using model-compound systems, under similar reaction conditions (T=400°C; P_r=1.1). We are also in the process of characterizing the toluene, methanol and water supercritical coal extracts by GPC and other analytical techniques, that will enable us to determine the differences in structure and functionality of these extracts.

3. Synergistic Effects of Solvent Mixtures

Possible non-ideal effects arising from polar/nonpolar solvent combinations were studied in supercritical extraction of coal at 400°C and constant total molar density for a series of toluene/methanol and toluene/acetone mixtures. Extraction yields and generated pressures are depicted in Figures 3 and 4.

Figure 3 for the toluene/methanol mixtures reveals a very interesting feature of the extraction curve, which passes through a maximum at a composition of approximately 70 mole% toluene and then descends slowly to the pure toluene value. This extraction maximum, which is higher than the extraction yield of either solvent alone (synergistic effect), is of even greater importance, because it is attained at a pressure much lower than the pressure generated in pure toluene extraction under similar conditions (3700 psig as compared with 5140 psig). Fong et. al. (8) observed a similar maximum-extraction effect in supercritical extraction of coal with toluene/methanol mixtures at 360°C and at a constant pressure of 2000 psig, but their results are of limited practical value, because of the constant-pressure condition that was employed (rather than constant solvent density).

Toluene/acetone mixtures, on the other hand, display almost linear dependence of both the extraction yield and the extraction pressure on molar composition. No synergistic effect is present under the given experimental conditions, so that pure toluene becomes a far superior supercritical solvent than pure acetone or any toluene/acetone mixture, effecting much higher coal extraction at a considerably lower extraction pressure.

4. Physical and Chemical Changes in Coal Structure during Supercritical Extraction

Table 5 gives proximate and ultimate analyses and heat content values for selected coal samples that were extracted with pure supercritical solvents under a variety of experimental conditions. The analysis of the raw coal that was used in all these experimental runs is also included.

The data show a drastic (more than 60% in most cases) reduction in the volatiles content and a consequent increase in the fixed-carbon content of the coal after supercritical extraction. The reduction in volatiles is accompanied by a significant increase in the C/H atomic ratio of the treated coal, thus indicating a progressive extraction of hydrogen-rich fractions from the coal matrix. It is interesting to note, however, that even at high extraction levels, the extracted coal retains most of its fuel value, as indicated by a moderate C/H ratio and a high heat-content value. For example, coal extracted with supercritical toluene at 400°C and at a solvent density of 6.75 moles/liter retains 94.7% of the specific heating value of the raw coal, despite a 36% extraction loss and a corresponding 61.7% loss of volatiles.

The data indicate, once again, that supercritical water may be one of the most promising solvents in supercritical coal extraction, affecting higher extraction yields at much lower heat-content and H/C losses (for the extracted coal) than hydrocarbon solvents (for example, compare the results of the pure toluene and the water runs).

A very interesting selective desulfurization effect is observed in supercritical extraction of coal with methanol-based solvents, and to a lesser extent with acetone and water. Ideally, if there is no special affinity of the supercritical solvent towards sulfur (or other heteroatom), the extraction of sulfur fractions from the coal matrix should be non-selective, so that the sulfur content of the extracted coal, as well as that of the extract, is in every case the same with the sulfur content of the raw coal. Our data show that, although this is true for nitrogen, sulfur undergoes strong selective extraction in the presence of methanol-based solvents.

Supercritical extraction of coal with pure methanol results in a 31.8% level of selective sulfur reduction, while the other two oxygenated solvents, acetone and water, also display significant (≈23%) desulfurizing action on extracted coal samples. Chemical participation of the methanol in the coal-pyrolysis stage, that enhances selectively the fragmentation of sulfur clusters in the coal molecule and their subsequent extraction in the supercritical phase is proposed to be the main cause of this effect.

Finally, surface areas of extracted coal samples were measured by nitrogen adsorption at -196°C to determine the effect of possible changes occuring in the physical structure of the coal during supercritical extraction. The results are given in Table 6. A sharp decrease in the available surface area of the coal is observed in all the extracted samples, and this decrease, at least for the paraffinic series, is progressively more pronounced at higher extraction levels. Methanol-extracted coal, on the other hand, shows a higher surface-area reduction than hexane-extracted coal, despite the lower extraction level. The surface-area-reduction effect may be attributed to a shift in the pore-size distribution of the coal caused by the extractive action of the supercritical solvent. The removal of coal material from the solid matrix may result in the progressive opening of larger pore spaces, thus shifting the pore-size distribution towards the macropore range, generally associated with low specific surface areas. Swelling phenomena in the coal matrix caused by strong H-bonding solvents, such as methanol, can contribute further to the closing of smaller pores and, thus, to additional collapse of the microporous network. Fong et. al. (8) proposed a different explanation based on the retention of extract in the pores. At the end of an extraction cycle, the removal of the volatile supercritical solvent from the pores could result in partial condensation of the coal extract and, thus, in extensive pore blockage.

Concluding this section we would like to report some results on the pyridine solubility of raw and extracted coal samples. The pyridine solubilities of dried samples were determined by stirring 0.5 grams in 50 cm^3 pyridine for 2 hrs at room temperature, then filtering and evaporating the solvent, and drying the solid residue under vacuum at 110°C for 24 hrs. Results for the raw coal and for the pure toluene and pure methanol runs are given below:

Supercritical Solvent	Extraction Conditions	Weight Percent Extraction	Pyridine Solubility of Extracted Coal (%)
RAW COAL			11.2
Toluene	400°C, 6.75 $\frac{\text{moles}}{\text{liter}}$	36.0	0.8
Methanol	400°C, 6.75 $\frac{\text{moles}}{\text{liter}}$	20.6	2.4

The pyridine solubility of coal decreases sharply after supercritical extraction, indicating that most of the coal material that is soluble in pyridine at room temperature dissolves in the supercritical solvent during the high temperature extraction.

It is also important to report here that part of the supercritical extract recovered in the toluene phase after cooling the reactor's contents to room temperature, is in the form of a precipitate, fully soluble in pyridine, and amounting to approximately 8 wt% on the basis of raw dry coal. Therefore, contrary to the claim of Blessing and Ross, a significant part of the coal material which is soluble in the solvent under supercritical conditions, becomes insoluble when the solvent is brought back to ambient conditions.

SUMMARY

The specific physical and chemical characteristics of supercritical solvents and solvent mixtures that can affect the yield and the properties of coal extracts were experimentally investigated. Strong non-ideal interactions, such as polar forces and hydrogen bonding, as well as synergistic interactions in multicomponent solvent mixtures, were shown to produce large deviations from the simple, density-driven supercritical solubility. These interactions can be manipulated to optimize supercritical coal extraction by reducing the severity of the extraction conditions (pressure in particular). Physical and chemical changes occuring in the coal structure during supercritical solvent extraction were also examined.

ACKNOWLEDGEMENTS

This work was supported by the United States Department of Energy under Grant No. DE-FG22-81PC40801 and by the Center for Energy Studies, Austin, Texas. The support of the two agencies is gratefully acknowledged.

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Table 1. Supercritical extraction of coal with a homologous series of n-paraffins at 400°C and at a (constant) solvent density of 2.75 $\frac{\text{moles}}{\text{liter}}$.

Solvent	Weight Percent Extraction	Extraction Pressure (psig)
Pentane	18.43	2032
Hexane	19.26	1635
Heptane	19.70	1441
Octane	20.70	1393
Nonane	21.17	1290
Decane	22.75	1380
Undecane	23.16	1562
Dodecane	23.56	1768

Table 2. Physical solvent parameters for the homologous series of n-paraffins from pentane to dodecane.

Solvent	Critical Temperature (°C)	Critical Pressure (atm)	Critical Density (g/cm^3)	a ($\times 10^9$)[1] ($\frac{cm^6 \cdot atm \cdot °K^{1/2}}{mole^2}$)	b[1] ($cm^3/mole$)	Extraction Pressure (psig)[2]	Solubility Parameter ($cal^{1/2}/cm^{3/2}$)[3]
Pentane	196.6	33.3	0.237	0.4137	100.36	1680.2	2.27
Hexane	234.2	29.9	0.233	0.5586	120.72	1531	2.61
Heptane	267.1	27	0.232	0.7238	142.35	1425.9	2.90
Octane	296	24.8	0.232	0.8977	163.27	1383.3	3.17
Nonane	321	22.5	0.231	1.1017	187.87	1492.5	3.42
Decane	344.4	20.8	0.231	1.3125	211.22	1755.3	3.65
Undecane	365.2	19.2	0.230	1.5446	236.53	2363.6	3.85
Dodecane	386	17.9	0.230	1.7951	261.98	3502.1	4.05

[1] Constants of the Redlich-Kwong equation of state

[2] Calculated from the Redlich-Kwong equation at the supercritical extraction conditions: 400°C, 2.75 moles/liter

[3] Calculated from Giddings' correlation at the supercritical extraction conditions: ρ = 2.75 moles/liter

Table 3. Extraction pressures calculated from the Redlich-Kwong equation of state at 400°C and two different solvent densities.

Solvent	ρ = 2 moles/liter		ρ = 3 moles/liter	
	Extraction Pressure(psig)	Solubility Parameter[1]	Extraction Pressure(psig)	Solubility Parameter[1]
Pentane	1236.2	1.65	1849.3	2.48
Hexane	1106.3	1.90	1713.3	2.85
Heptane	978.8	2.11	1650.7	3.16
Octane	863.1	2.31	1687.4	3.46
Nonane	771.8	2.49	1974.5	3.73
Decane	705.9	2.65	2538.0	3.98
Undecane	690.8	2.80	3757.3	4.2
Dodecane	727.1	2.95	6239.7	4.42

[1] Calculated from Gidding's correlation

Table 4. Supercritical extraction of coal with various solvents at 400°C.

Solvent	Weight Percent Extraction	Extraction Pressure[1] (psig)	Solvent Density[1] ($^{moles}/_{liter}$)	Solubility Parameter[2]
Toluene	36.0	5140	6.75	6.46
"	27.6	1440	4.0	3.83
"	20.3	1260	2.75	2.63
Acetone	4.0	2180	4.0	2.69
"	7.3	3480[3]	5.5	3.70
Methanol	20.6	3610	6.75	3.31
Water	34.0	3580	8.25	3.17
"	29.5	3070	7.08	2.72

[1] Experimental value

[2] Calculated from Giddings' correlation

[3] Significant decomposition of acetone was observed

TABLE 5. Proximate and ultimate analyses of coal samples extracted with supercritical solvents at 400 °C

Solvent Supercritical Density ($\frac{moles}{liter}$) Weight Percent Extraction	RAW COAL	Pentane 2.75 18.43	Octane 2.75 20.70	Dodecane 2.75 23.56	Toluene 4.0 27.6	Toluene 6.75 36.0	Methanol 6.75 20.6	Acetone 4.0 4.0	Water 7.08 29.5
Proximate Analysis[1] (%)									
Volatiles	42.3	21.9	24.0	25.4	21.6	25.3	24.6	23.1	18.1
Fixed Carbon	43.6	59.4	58.0	55.4	58.0	53.4	57.5	60.4	64.0
Ash	14.1	18.7	18.0	19.2	20.4	21.3	17.9	16.5	17.9
Ultimate Analysis[1] (%)									
Carbon	62.9	62.2	62.8	67.8	61.8	63.6	56.9	53.2	55.6
Hydrogen	4.7	3.5	3.5	3.7	3.1	3.1	3.6	3.7	3.2
Nitrogen	1.1	1.1	1.1	1.2	1.1	1.1	1.1	0.8	1.0
Sulfur	4.4	4.1	4.1	4.2	4.1	3.9	3.0	3.4	3.4
Oxygen (by difference)	26.9	29.1	28.5	23.1	29.9	28.3	35.4	38.9	36.8
Heating Value (Btu/lb)	11415	11560	11150	11510	10980	10805	11690	12280	11510
C/H ratio	1.11	1.48	1.50	1.53	1.66	1.71	1.32	1.20	1.45
% Sulfur reduction	0	6.8	6.8	4.5	6.8	11.4	31.8	22.7	22.7

[1]On a dry basis

Table 6. Nitrogen-surface areas of coal samples extracted with various supercritical solvents at 400 °C.

Solvent	Raw Coal	Hexane	Decane	Undecane	Dodecane	Methanol
Supercritical density ($\frac{moles}{liter}$)	–	2.75	2.75	2.75	2.75	6.75
Weight percent extraction	0	19.3	22.8	23.2	23.6	20.6
N_2 surface area (m^2/g)	38.4	12.7	3.0	2.5	2.4	1.6
Surface-area reduction (%)	0	66.9	92.2	93.5	93.8	95.8

HOMOLOGOUS SERIES OF N-PARAFFINS

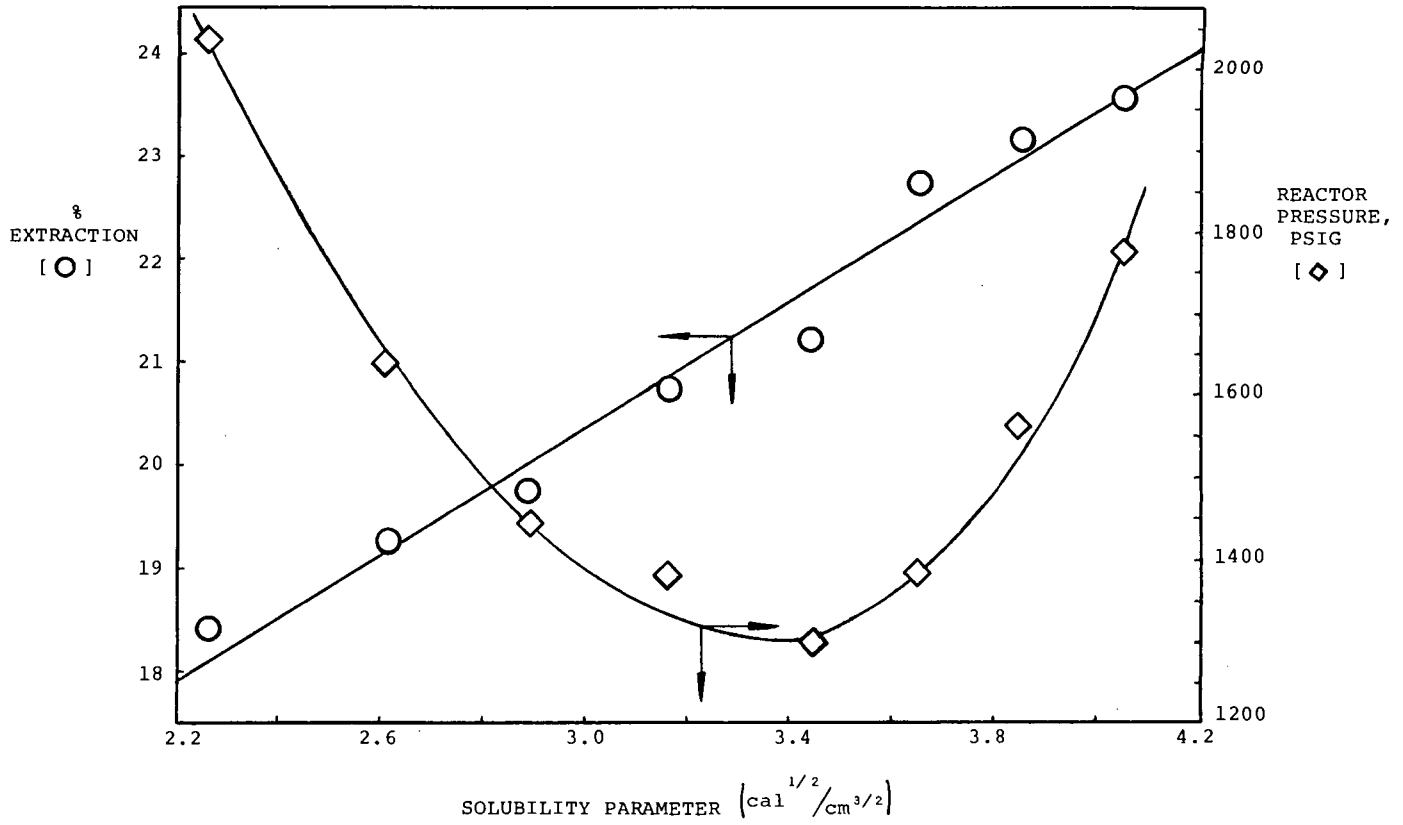

FIG. 1

TOLUENE-METHANOL MIXTURES

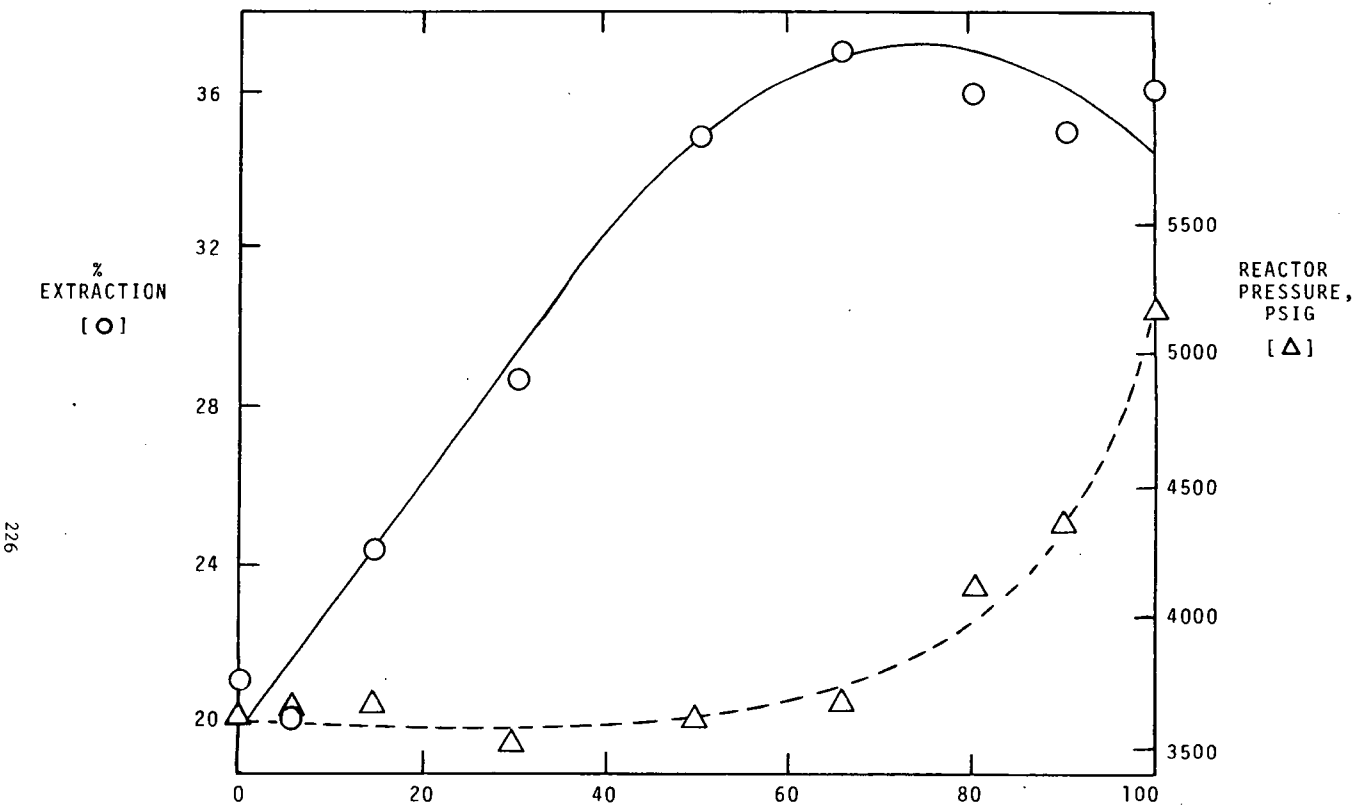

FIG. 2

TOLUENE-ACETONE MIXTURES

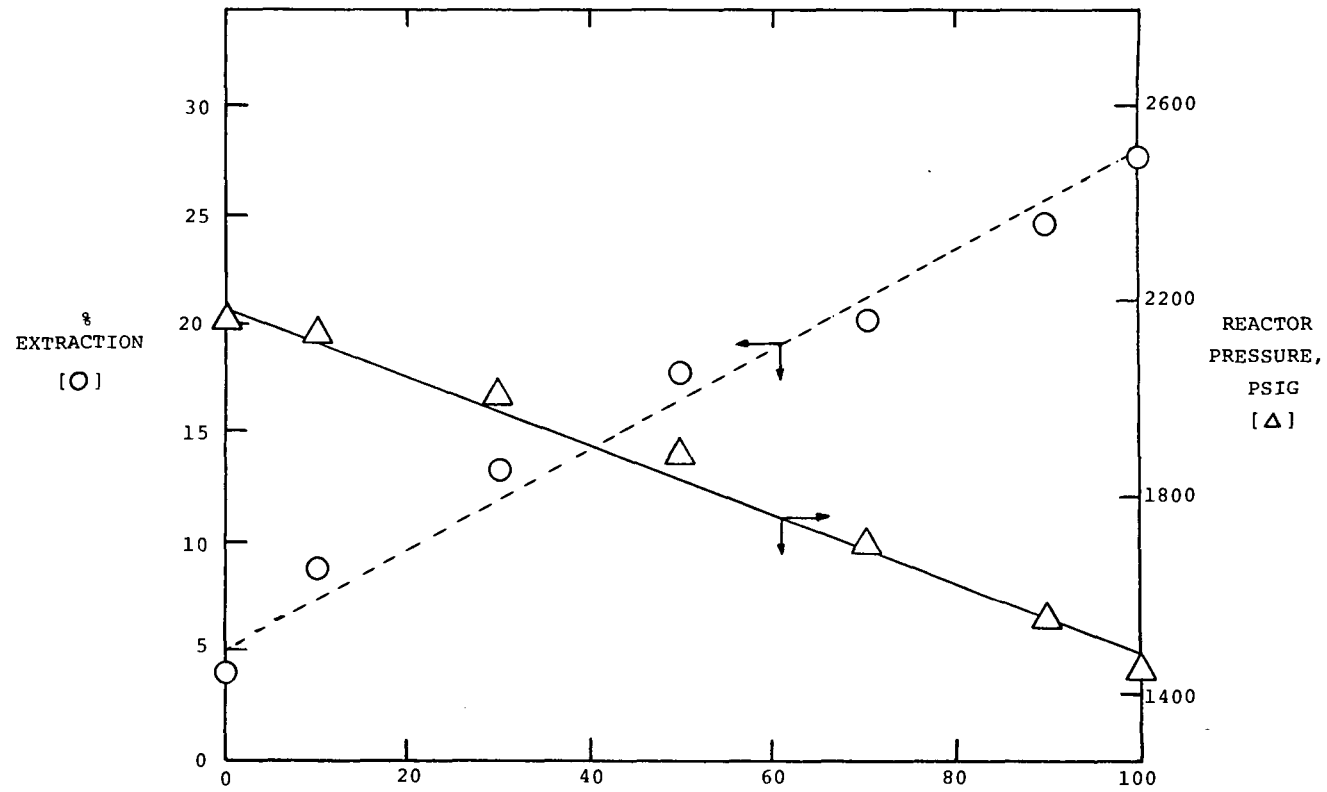

FIG. 3